

# Chemical Aspects of Actinides in the Geosphere: Towards a Rational Nuclear Materials Management

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# **Chemical Aspects of Actinides in the Geosphere: Towards a Rational Nuclear Materials Management**

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## **Overview:**

A complete understanding of actinide interactions in the geosphere is paramount for developing a rational Nuclear and Environmental Materials Management Policy. One of the key challenges towards understanding the fate and transport of actinides is determining their speciation (i.e., oxidation state and structure). Since an element's speciation directly dictates physical properties such as toxicity and solubility, this information is critical for evaluating and controlling the evolution of an actinide element through the environment. Specific areas within nuclear and environmental management programs where speciation is important are 1) waste processing and separations; 2) wasteform materials for long-term disposition; and 3) aqueous geochemistry.

The goal of this project was to develop Actinide X-ray Absorption Spectroscopy (XAS) as a core capability at LLNL and integrate it with existing facilities, providing a multi-technique approach to actinide speciation. XAS is an element-specific structural probe which determines the oxidation state and structure for most atoms. XAS can be more incisive than other spectroscopies because it originates from an atomic process and the information is always attainable, regardless of an element's speciation. Despite the utility, XAS is relatively complex due to the need for synchrotron radiation and significant expertise with data acquisition and analysis. The coupling of these technical hurdles with the safe handling of actinides at a general user synchrotron facility such as the Stanford Synchrotron Radiation Facility (SSRL) make such experiments even more difficult. As a result, XAS has been underutilized by programs that could benefit by its application.

We achieved our project goals by implementing key state-of-the-art Actinide XAS instrumentation at SSRL (Ge detector and remote positioning equipment), and by determining the chemical speciation of actinides (Th, U, and Np) in aqueous solutions, wasteform cements, and with geologic materials. The results provide a rational scientific basis for ongoing DOE projects involving nuclear and environmental materials challenges. Future LLNL projects will utilize the Actinide XAS expertise to characterize actinides in important chemical systems, while continuing to improve the XAS capabilities to study metallic alloys, cryogenic sample conditions, and lower analyte concentrations.

## **1. Neptunium Speciation in Solubility Experiments.**

Of the constituents present in spent nuclear fuel,  $^{237}\text{Np}$  is of particular concern because it is the primary source of radiological hazard to the biosphere for waste storage times in excess of 10,000 years. Compounding the long half-life of this

isotope is neptunium's preference to present itself in the Np(V) oxidation state under oxidizing environmental conditions. This oxidation state tends to be more soluble than Np(IV) in aqueous solutions and less strongly sorbed by geologic material surrounding a nuclear waste repository (e.g. Yucca Mountain).

In our first XAS measurements, we studied a series of Np solid precipitates. These compounds were prepared in related experiments conducted to study the solubility and thermodynamic stability of Np at Yucca Mountain. In comparing the Np L<sub>III</sub>-edge XAS Fourier Transforms (FTs) for the Np(V) species  $\text{NpO}_2^+$ , the Np(IV) solid compound  $\text{NpO}_2$ , and one of the solid Np precipitates, we observed a change in Np speciation for the precipitate. The bonding patterns demonstrate that the Np precipitate has a local structure similar to that of the known tetravalent Np compound  $\text{NpO}_2$ . This is interesting because the starting material for the solubility experiment was composed of the pentavalent Np species ( $\text{NpO}_2^+$ ,  $\text{O}=\text{Np}=\text{O}$ ) possessing a dramatically different local bonding pattern. The detection of Np(V)→Np(IV) transformation may prove to be important for understanding the fate of Np at Yucca Mountain.

## **2. Neptunium Sorption on Cementitious Materials.**

Concrete structures will be present in significant amounts in the proposed nuclear waste repository at Yucca Mountain. Over the long term, leaching from waste forms may lead to actinide interactions with the surrounding cementitious materials. As a result, it is important to understand the nature and level of interactions of actinides with these materials in order to evaluate, predict, and control transport. During FY99, we investigated the behavior of the Np(V) ion in the presence of these materials using XAS. Measurements were performed at the Stanford Synchrotron Radiation Laboratory (SSRL) by probing the Np L3 absorption edge for Np-loaded cement samples in-situ. We observed strong interactions with the cement materials, suggesting that the concrete structures will act as an additional barrier to actinide migration at high pH. In addition, we observed a chemical reduction of Np(V) to Np(IV) over time. Since tetravalent Np species are significantly less soluble than pentavalent Np species, this may be a fundamental controlling condition for decreased mobility of Np within the repository.

## **3. Uranium Sorption on Alumina, Silica, and Montmorillonite.**

With respect to migration in the far field, actinide ions may have the propensity to interact with certain minerals and clays. We have investigated the adsorption of the uranyl ion ( $\text{UO}_2^{2+}$ ) in contact with silica ( $\text{SiO}_2$ ), alumina ( $\text{Al}_2\text{O}_3$ ), and montmorillonite surfaces in the pH range of 3.1-6.5, using XAS spectroscopy to observe the local structure around the uranium atom. Analysis shows that in all samples the uranyl ion structure is preserved, with two axial oxygen atoms detected at ca. 1.8 Å. For the montmorillonite samples at low pH a single equatorial oxygen shell is observed at ca. 2.4 Å, with a coordination number of  $6\pm1$ . At high pH (6.41) and high ion concentration (0.1 M NaCl), two separate equatorial shells are observed with bond lengths of ca. 2.30 and 2.48. The samples of uranyl on silica and alumina are all observed to have two separate equatorial shells with bond lengths of ca. 2.30 Å and 2.49 Å. A uranium shell at ca. 4.0 Å is observed in the high pH (~6.5) samples of uranyl on silica and on alumina. A silicon shell at ca. 3.10 Å is observed in the sample of uranyl on silica at pH 6.5.

These results suggest that adsorption of the uranyl ion onto montmorillonite at low pH is occurring via ion exchange, leaving the inner-sphere uranyl structure intact. At high pH and in the presence of a competing cation, inner-sphere complexation with the surface occurs predominates. Adsorption of the uranyl onto the silica and alumina surfaces appears to occur via an inner-sphere, bidentate complexation with the surface, with the formation of polynuclear complexes occurring at higher pH.

#### 4. Uranium and Thorium Complexation Studies with Tiron

We have determined the structure of uranyl,  $\text{UO}_2^{2+}$ , and  $\text{Th}^{4+}$  complexes formed in aqueous solution with pyrocatechol-3,5-disodium sulfonate (Tiron) as function of pH and concentration. Tiron complexation is a potential soil-remediation method, and Tiron is known to be an effective complexing agent. At equimolar concentrations of 0.05 M  $\text{UO}_2^{2+}$  and Tiron the predominant species was found to be aqueous uranyl at pH = 2.0. With increasing pH up to pH = 6.0, the formation of a 3:3  $\text{UO}_2^{2+}$ :Tiron trimer was observed. In this structure, bidentate catecholate complexation to Tiron as well as oxygen bridging between uranyl units is detected.

For thorium structural changes were observed both as a function of pH and Th:Tiron (Th:L) ratio. At Th:L = 1:1 and pH = 1.4, a monomeric complex is observed with each Th center complexing monodentate to ~1 sulfate functional group. At pH 4.0 similar sulfate ligation is observed along with oligomer formation. At pH 6.0 a thorium hydrolysis oligomer is formed, with no evidence for inner-sphere Tiron coordination.

When Th:L is changed to 1:2 at pH = 6.0, an unusually stable complex is formed that remains favored over hydrolysis for Th:L ratios up to 1:5. This complex is characterized by bidentate catechol and monodentate sulfate ligation to Tiron and oxygen bridging between thorium atoms, and is consistent with the formation of the 2:3 Th:L complex proposed from earlier studies. At a Th:L ratio of 1:10, Th complexation is dominated by bidentate catechol ligation and the formation of a monomeric  $\text{Th}(\text{Tiron})_x$  species. The structural determination of these complexes is crucial for the correct thermodynamic modeling of actinide-Tiron complexation and identifies the catecholate groups as active chelating agents.

#### Publications:

- Sylwester E. R., Hudson E. A., Allen P. G. (2000): The Structure of Uranium (VI) Sorption Complexes on Silica, Alumina, and Montmorillonite. *GEOCHIM. ET COSMOCHIM ACTA*. **64**, 2431-2438. UCRL-134461
- Zhao P., Allen P. G., Sylwester E. R., Viani B. E. (2000): The Sorption of Uranium(VI) and Neptunium(V) onto Hydrothermally Altered Concrete. *RADIOCHIM. ACTA*. **88**, 729-736. LLNL Report, UCRL-VG-135790.
- Sylwester, E. R., Hudson, E. A., Allen, P. G. (2000): Surface Interactions of Actinide Ions with Geologic Materials Studied by XAFS. *PROC. MAT. RES. SOC.*, **590**, 9-16. UCRL-135790
- Sylwester E. R., Allen P. G., Zhao P., Viani B. E., (2000): Interactions of Uranium and Neptunium with Cementitious Materials Studied by EXAFS. *PROC. MAT. RES. SOC.*, **608**, 307-312.

- Sylwester, E. R., Allen, P. G., Dharmawardana, U., Sutton, M. (2001): Structural Studies of Uranium and Thorium Complexes with 4,5-dihydroxy-3,5-benzenedisulfonate (Tiron) at Low and Neutral pH by X-Ray Absorption Spectroscopy. INORG. CHEM. (submitted Jan 2001).
- Hakem N., Allen P. G., Sylwester E. R. (2000): Effect of EDTA on Plutonium Migration. LLNL Report UCRL-JC-139652.
- Hakem N., Allen P. G., Sylwester E. R. (2000): Sorption and Diffusion Studies of Pu(IV) And Pu(IV)-EDTA onto and through Hanford Soil. LLNL Report, UCRL-JC-135799.

#### **Refereed Presentations:**

- Allen, P. G. "Structural Characterization of Trivalent Actinide and Lanthanide Ions in Concentrated Chloride Solutions by XAS." J. J. Bucher, N. M. Edelstein, and D. K. Shuh, Symposium on Heavy Element Complexes, ACS National Meeting, Anaheim, Mar. 1999.
- Allen, P. G. "Applications of XAFS Spectroscopy to Speciation Problems in Environmental Radiochemistry." D. K. Shuh, J. J. Bucher, N. M. Edelstein, and T. Reich. Euro-Conference and NEA Workshop on Speciation, Techniques, and Facilities for Radioactive Materials at Synchrotron Light Sources, Grenoble France, Oct. 1998.
- Sylwester, E. R. "Structural studies of U(VI) and Th complexes with pyrocatechol-3,5-disodium sulfonate (tiron) at low and neutral pH." American Chemical Society Western Regional Meeting, San Francisco, Oct. 2000.
- Sylwester, E. R. "Interactions of Uranium and Neptunium with Cementitious Materials Studied by XAFS." American Chemical Society Meeting, San Francisco, Mar. 2000.
- Sylwester, E. R. "Surface Interactions of Actinide Ions with Geologic Materials Studied by XAFS." Materials Research Society Meeting, Boston, Nov. 1999.
- Sylwester, E. R. "Structure of Uranium(VI) Sorption Complexes on Silica, Alumina, and Montmorillonite." Poster. 7<sup>th</sup> Int. Conference on Chemistry and Migration Behavior of Actinides and Fission Products in the Geosphere (Migrations '99). Incline Village, NV, Oct 1999
- Sylwester, E. R. "Interactions of Uranium and Neptunium with Cementitious Materials Studied by XAFS." Poster, SSRL Users' Conference. Stanford, CA, Oct 1999.

#### **Invited Talks:**

- Allen, P. G. The Role of Actinide XAS in Environmental Studies Applicable to Yucca Mountain and the Nevada Test Site. SSRL Users Conference, October 2000.
- Allen, P. G. XAFS Spectroscopy of Actinides in the Solid State. Euro-Conference and NEA Workshop on Speciation, Techniques, and Facilities for Radioactive Materials at Synchrotron Light Sources, Grenoble France, Sept. 2000.
- Allen, P. G. Structural Characterization of Actinide Catechol Complexes by EXAFS. Talk delivered at Forschungszentrum Karlsruhe, Institute for Radiochemistry, Karlsruhe Germany, Sept 2000.
- Allen, P. G. Surface Interactions of Actinide Ions with Geologic Materials Studied by XAFS. P. G. Allen, E.R. Sylwester, E.A. Hudson. Symposium on Applications of

Synchrotron Radiation Techniques to Materials Science. MRS Fall Meeting, Boston 1999.

Allen, P. G. Nuclear Waste Studies By The Seaborg Institute At LLNL. Guest Lecture Delivered at Mass. Inst. of Tech., Dept. of Nucl. Eng. Dec. 2, 1999.

Allen, P. G. Experimental Procedures and Safety Considerations for Transuranic Studies at the Stanford Synchrotron Radiation Laboratory. D. K. Shuh, J. J. Bucher, N. M. Edelstein, and T. Reich. Euro-Conference and NEA Workshop on Speciation, Techniques, and Facilities for Radioactive Materials at Synchrotron Light Sources, Grenoble France, Oct. 1998.